Hybrid Perovskite Solar Cells

The Genesis and Early Developments

2009-2014

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Chapter 1
Introduction

The goal of science is understanding and control on our environment. Perhaps one of the most fascinating aspects of the sciences is that moment when a radical novelty appears, attracting full attention of a broad array of scientists. It is a colonization of a new territory that is not physical as earth, but is material and real. Under the expectation that there will be many unexplored aspects where you can apply your tools, or have an occasion to develop new ones, many feel compelled to jump in before it is too late and very crowded. There is a large driving force for uncovering the appealing unknown and suddenly all the major factors of the complicated machinery of science seem to be favorably aligned in a specific direction and well-oiled for operation. The world of scientific publication, the commissions adjudicating projects, the Institutes in search of researchers, all the gatekeepers become friendly and the different resource-controlling domains start giving high incentives to those early contributors, which will drive to the cause yet more practitioners, in a self-sustaining glowing process. This is what is called a "hot topic". One may wonder if the rush for novelty is positive after all in the sense of the scientific endeavor as seen from a more general and historical perspective. Nowadays one can only say that this is how the scientific world functions, and maybe it was not so differently in the past, but only the communications were slower. Nevertheless the polarization of a vast quantity of people and large amounts of resources around a hot topic, does have the virtue to rapidly generate a large community able to attack a subtle and difficult new research subject. The establishing of a scientific opinion is an intricate process, requiring complex and dedicate work in multiple aspects, confrontation of ideas, and robust and scholarly reporting and discussion, before all is clear, digested, and easy to learn. Being able to replicate, reproduce, and disprove, is essential for the advancement of established knowledge. A generous quantity of experienced and starting scientists, labs, and resources, devoted to a single goal, makes progress to be fast, sound, and firmly based.

In this book we tell the history of one of such moments, that occurred mainly around the years 2012-2014, and which led to the development of the lead halide perovskites as a top class material for solar cells.

Solar energy is a very abundant and distributed resource that surpasses in great excess any human energy needs that may be forecasted, Fig. 1.1A. However, the conversion of incoming solar radiation to electricity is a challenging process. One key branch of solar energy research, the field of photovoltaics, consists on the investigation of materials and their combinations suitable to form devices that convert the sunlight into electricity. The main limitation for the widespread use of photovoltaic energy conversion that can be overcome by scientific and technological work, is the cost and availability of materials, and the processes leading to stable and reliable devices.

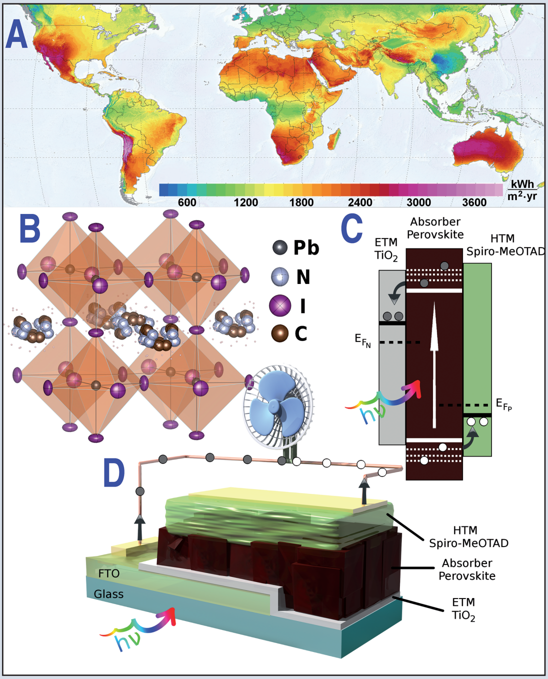

Figure 1.1: According to the CIA World FactBook 2017, average and median world electric energy consumption are 2674 and 1927 kW h per person per year, respectively. Electricity consumption is country dependent and the consumption range spans from 50613 kW h/(person year) consumed in a first world country as Iceland to less than 8 kWh/(person year) in Chad Republic. Direct normal sun irradiation on Earth surface as accumulated in one year per square meter is shown in the map (A) (GHI Solar Map © 2017 Solargis.) It is impressive that many countries in the world could obtain their average electric energy necessities per person per year only using one/two meter square of their land domains. (B) Tetragonal crystal structure of $CH_3NH_3PbI_3$ perovskite as determined from XRD measurements in single crystal (ref no. 238610, Inorganic Crystal Structure Database). In contrast with the conventional way of representing lonely methylammonium organic cation in A position of this perovskite, here methylammonium organic cation is partially occupying 8 equivalent positions in its cavity. (C) Simplified energy band scheme for perovskite solar cell stack showing hybrid perovskite absorber material sandwiched between electron transport material (ETM, TiO_2) and hole transport material (HTM, Spiro-MeOTAD). After higher energy than perovskite band gap photons are absorbed in the material, electrons and holes are promoted to the respective conduction and valence bands. Selective contacts for electrons and holes separate and extract charge from the absorber. Adapted from The Physics of Solar Cells: Perovskites, Organics, and Photovoltaic Fundamentals. J. Bisquert. 2017 CRC Press. (D) Perovskite solar cell conventional stack section using glass, FTO, TiO_2 compact layer, perovskite absorber and Spiro-MeOTAD layer. Holes are extracted from the Spiro-MeOTAD side and electrons from TiO_2 compact layer side. Both meet again on the load in this case represented by a fan closing the electric circuit.

A central feature of the solar energy conversion is the power conversion efficiency of a given class of materials. A promising conversion figure is when 5% of the whole energy contained in the photons of the solar spectrum, is transformed to electrical energy flowing out of the terminal wires in the device in terms of electrical current at a certain voltage. However, a material prepared in research labs must ultimately become a profitable technological reality for extensive diffusion in the market and effective utilization in the society. A low efficiency of conversion will demand a larger panel area to produce a featured quantity of power. Thus, anything far below 20% power conversion efficiency is considered a lesser competitor for massive energy production (though lower conversion efficiencies may be suitable for niche markets).

For many years along the 20th century photovoltaic research and technology was dominated by a few types of inorganic semiconductor compounds, headed by the crystalline silicon, that were found to provide a very good energy conversion ratio. It has been noted several decades ago that crystalline photovoltaic materials such as silicon, the most spread material in installations, and gallium arsenide, best performing material ever found, have the inconvenient that they demand a nearly perfect crystal structure that must be formed in large facilities involving expensive and high temperature procedures. Naturally there was extensive search for other suitable compounds that would decrease the strict requirement of a massive crystal occupying the full size of the semiconductor slab, and some polycrystalline materials that could be deposited on a substrate forming thin film large area devices, such as cadmium telluride, where amply investigated in the 1980s. The learned lesson of these endeavors was that a large research community could bring a promising material from the initial to the effective 20% value in about 20 years of sustained effort of investigation. The slow pace of development of the main past technologies is shown in the table of record efficiencies measured under strict calibration procedures, published by the National Renewable Energy Laboratory (NREL), shown in Fig. 1.2.

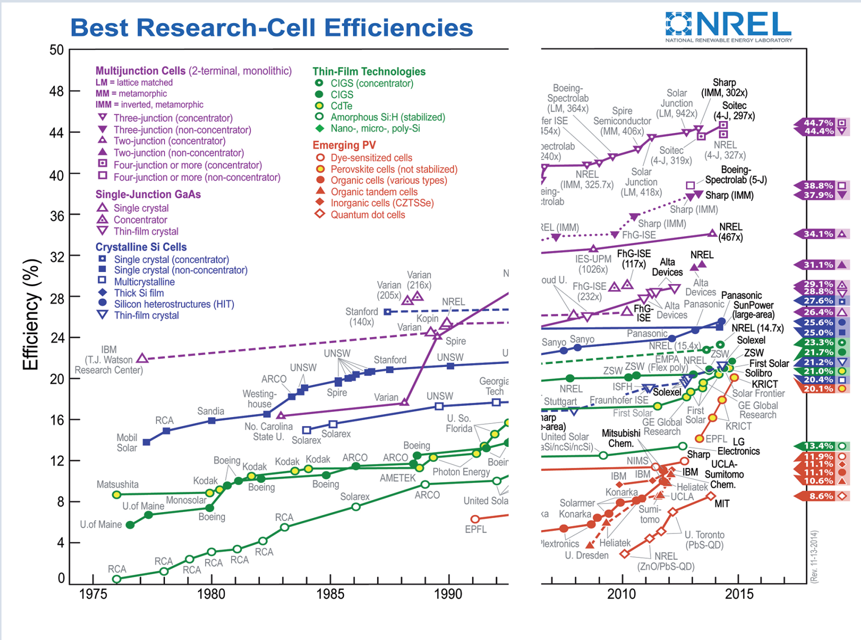

Figure 1.2: Best solar cells certified efficiencies published by NREL.

In the early 1990s a series of radically new materials and devices approaches were adopted that eventually led to mainstream research topics. First, the dye-sensitized solar cells (DSC) emerged from previous methodologies in photoelectrochemistry. An organic dye would be anchored to electron transporter TiO_2 semiconductor mesoporous matrix, ensuring a large internal area for full harvesting of the solar spectrum. Here the circuit was closed by a redox electrolyte and a counterelectrode. On the other hand the development of optically active conducting polymers translated into the first full organic solar cells consisting on a combination of electron donor-acceptor couple materials forming an effective structure for charge generation and extraction.